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GROWTH OF GaAs CRYSTALS BY THE HEAT EXCHANGER METHOD (HEM™) FOR MICROWAVE DEVICE APPLICATIONS

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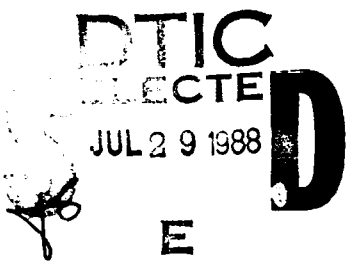

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Large GaAs crystals with uniform properties and low defect density are required for microwave devices. The variable quality of the available GaAs, wafer-to-wafer, intra-wafer, boule-to-boule, and intra-boule is unsatisfactory for high yield device processing. It has been shown that undoped (100) semi-insulating GaAs crystals can be grown using the Heat Exchanger Method (HEM™) with remarkably uniform electronic properties. It has also been demonstrated that undoped dislocation-free GaAs crystals can be grown by HEM.

The present effort was to understand the cause of lineage and twinning observed in the structure of 3-inch-diameter GaAs boules. Twinning is caused by non-optimized seeding conditions. By adjusting the crystal growth parameters, optimum seed meltback has been obtained and twinning has been eliminated in initial growth. Characterization for carrier concentration, EL2 and mobility has shown remarkable uniformity within the boule. Undoped semi-insulating 3-inch-diameter (100) GaAs grown by HEM has shown mobility in excess of 7,000 $cm^2/V.sec$ which is higher than state-of-the-art commercially available GaAs. Mapping of EL2 concentration within a 3-inch-diameter wafer has shown a mean value of $1.58 \times 10^{16}/cm^3$ with a standard deviation of less than 1.2 percent. The carbon concentration in HEM GaAs is below detectability limit ($<3 \times 10^{14}/cm^3$). The potential for producing GaAs crystals by HEM with uniform properties for microwave applications has been demonstrated.

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Preface

The program entitled "Growth of GaAs Crystals by the Heat Exchanger Method (HEM™) for Microwave Device Applications" was carried out at Crystal Systems, Inc. under the sponsorship of Air Force Wright Aeronautical Laboratories, Materials Laboratory (AFWAL/MLPO), Wright-Patterson AFB, OH 45433-6533.

Dr. Chandra Khattak was the Principal Investigator and Frederick Schmid was the Program Manager. The Technical Monitor was Donald Evans and the Contracting Officer was Tony Everidge.

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1.0 Introduction

Gallium arsenide (GaAs) crystals are required as substrates for fabrication of microwave devices. Amplifiers and monolithic integrated circuits based on GaAs are finding increased use in military systems. The variable quality of available GaAs (wafer-to-wafer, intra-wafer, boule-to-boule, and intra-boule) is unsatisfactory for high-yield device processing. Large GaAs crystals with uniform properties and low defect densities are required to improve microwave devices fabricated for military systems.

Currently, two crystal growth processes are being used commercially for the production of GaAs crystals; viz., the Liquid Encapsulated Czochralski (LEC) and the Horizontal Bridgman (HB) techniques. While the LEC process produces the desired semi-insulating properties without doping, the defect density in these crystals is high and non-uniform. The electrical properties and defect density across the LEC wafer show a W-shaped distribution. Conversely, the HB process produces a lower defect density; however, it is necessary to dope the crystals in order to achieve semi-insulating properties. Further, the orientation of HB crystals grown commercially is (111) and only D-shaped (100) orientation wafers are obtained by angle cutting them from the boule.

Efforts have been made in the industry to develop the growth of low defect density LEC wafers[1-8]. Indium-doped GaAs crystals have shown the best results. Although the defect density is reduced, indium-doped GaAs wafers exhibit growth striations due to the low segregation coefficient of indium[9], and these wafers are not suitable for microwave devices. Therefore, it is desirable to develop a technique to grow ingots with low defect density that will yield uniform inter- and intra-wafer electrical uniformity.

We have demonstrated[10] that GaAs wafers produced by the Heat Exchanger Method (HEM™) exhibit remarkable consistency in properties across a 5-cm-diameter wafer. The carrier concentration, EL2 concentration, and mobility of HEM GaAs show less than 5 percent variation across a 5-cm-diameter wafer. Further, we have demonstrated[10] that undoped dislocation-free GaAs crystals can be grown by HEM. These crystals exhibit semi-insulating properties even when grown in silica crucibles. The HEM growth has been extended to 3 inches diameter. It is observed[11] that the characteristics of the 3-inch-diameter wafers are similar to those of the 2-inch wafers. The uniformity of carrier concentration, EL2 and mobility, axially and radially, found in the 2-inch-diameter boules also exists in the 3-inch-diameter boules. However, lineage and twinning are observed in the structure of the 3-inch-diameter boules. The lineage is associated with incomplete seeding at the outer edge of the seed.

A 6-month Phase I SBIR program was undertaken to optimize seeding parameters for 3 inches diameter GaAs crystal growth using HEM. It was intended to produce undoped 3-inch-diameter GaAs boules and evaluate the crystals for uniformity in carrier concentration, EL2 and mobility across the wafers. At the start of the program the HEM furnace was set up to achieve higher temperature gradients in the solid during growth. In the HEM, it is not possible to observe seeding because of the submerged solid-liquid interface. The seeding parameters are therefore optimized with successive growth experiments. Once these parameters are established, they can be reproduced in the HEM furnace. At the start of the program the seeding step was non-optimum so that spurious nucleation and twins were observed in the structure. The seeding parameters were varied during the program so that nearly single crystal structure with minimal twinning was produced. Samples from various ingots were characterized for uniformity of electronic properties, and we have shown that the resistivity, carrier concentration, mobility and EL2 concentration are uniform within the boule. Undoped, semi-insulating ingots with mobilities greater than 7,000 $cm^2/V.sec$ have been produced. The feasibility of growing undoped 3-inch-diameter GaAs ingots in silica crucibles by HEM with uniform properties for microwave applications has been demonstrated.

2.0 Background

2.1 GaAs Crystal Growth

Two conventional technologies used for the growth of GaAs crystals are Liquid Encapsulated Czochralski (LEC) and the Horizontal Bridgman (HB) methods. In the HB method, GaAs crystals are grown in a horizontal configuration, and the crystals are typically grown in the (111) orientation. The (100) wafers fabricated from such boules are not circular.

The HB process has been modified so that (100) circular wafers can be cored perpendicular to the growth direction of horizontally grown crystals[12]. While this approach solves the shape problem of HB crystals, the uniformity of properties within the wafer and yield of material is still a problem[12]. These crystals are intrinsically not semi-insulating due to impurities. The major contaminant is usually silicon from the silica ampule and/or the boat. Semi-insulating GaAs crystals are obtained by the addition of chromium to the melt to compensate for the silicon impurity. During device processing, the chromium migrates due to the high diffusion coefficient, and thermal conversion is observed.

In the LEC process, the GaAs crystal is pulled from the melt through a B_2O_3 encapsulant which minimizes arsenic loss. Undoped semi-insulating GaAs crystals of circular cross section are obtained. However, high temperature gradients are necessary for growth, resulting in high dislocation densities, typically 10^4 to $10^5/cm^2$. The LEC process has been modified to grow crystals within a magnetic field using a very thick B_2O_3 layer and indium

doping[13]. Such crystals are grown in limited length and with poor diameter control. Further, indium has a very low segregation coefficient causing a large variation of indium concentration along the length of the boule[14]. Growth striations are also observed[15] within the wafer, thus complicating microwave device performance.

The HEM has been adapted for the growth of GaAs crystals[10,11,16]. The carrier concentration, mobility, and EL2 concentration for a 5-cm-diameter wafer is shown in Figure 1. The remarkable uniformity is far superior to radial variations of electronic properties in standard[17] LEC GaAs. Note that the uniformity of these properties extends across the whole HEM wafer and does not exhibit the W-shaped distribution characteristics of LEC wafers. This feature would allow use of the entire HEM wafer for device fabrication as opposed to LEC wafers where desirable properties are contained in the annular region. In addition to radial uniformity of HEM wafers, there is similar axial uniformity within the HEM boules.

We have observed that with HEM growth of GaAs, the dislocation density decreases with continued growth. Near the top of the ingot, the EPD can be reduced up to two orders of magnitude as compared to the EPD near the seed end. Reference 10 shows that the EPD of HEM GaAs has been limited by the EPD of the seed crystals. For an unseeded undoped crystal grown by HEM, the EPD distribution is shown in Figure 2. The EPD distribution profile is U-shaped, unlike the W-shaped characteristic observed for LEC GaAs. The EPD for HEM GaAs shown in Figure 2 is less

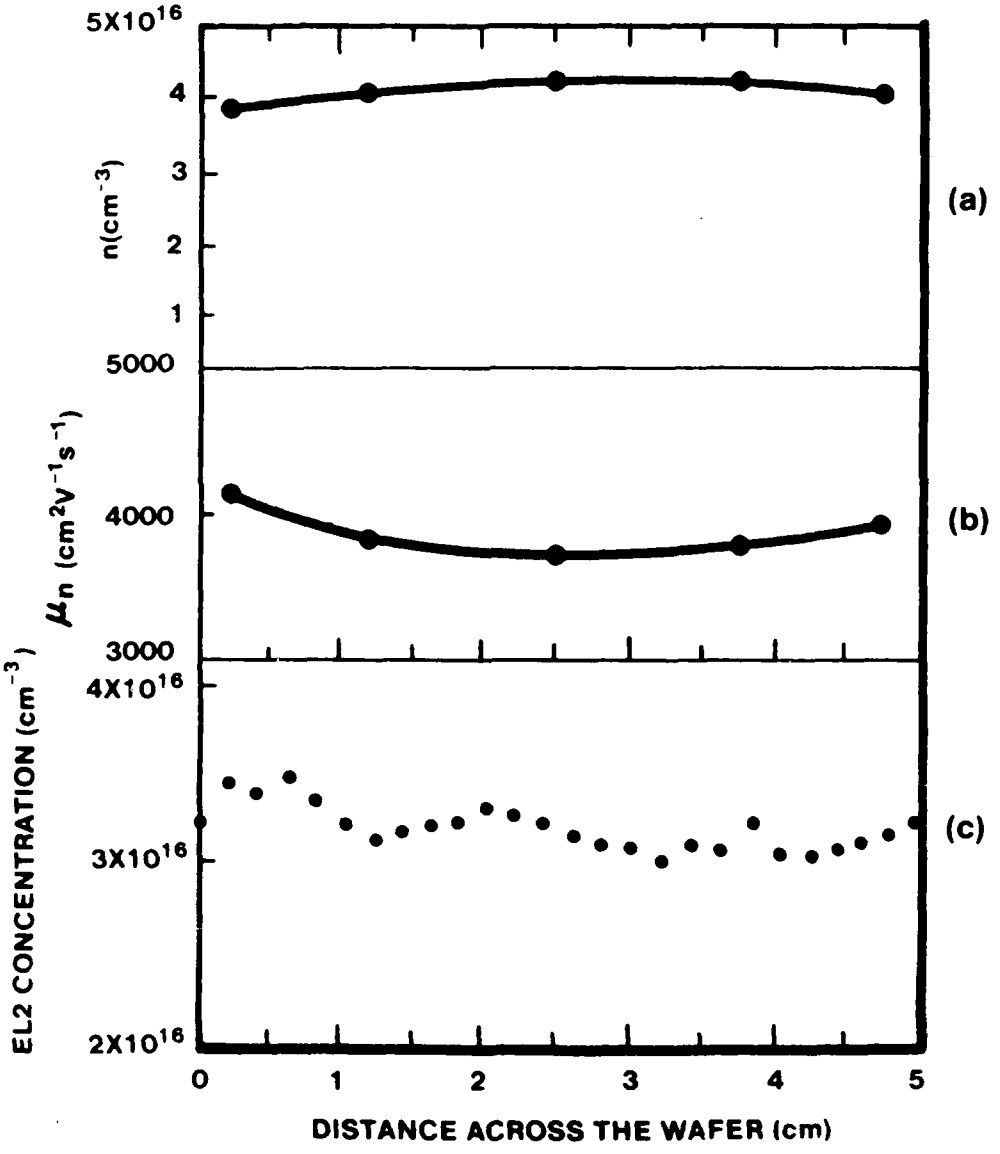


Figure 1. Uniformity of properties across a 5-cm wafer.

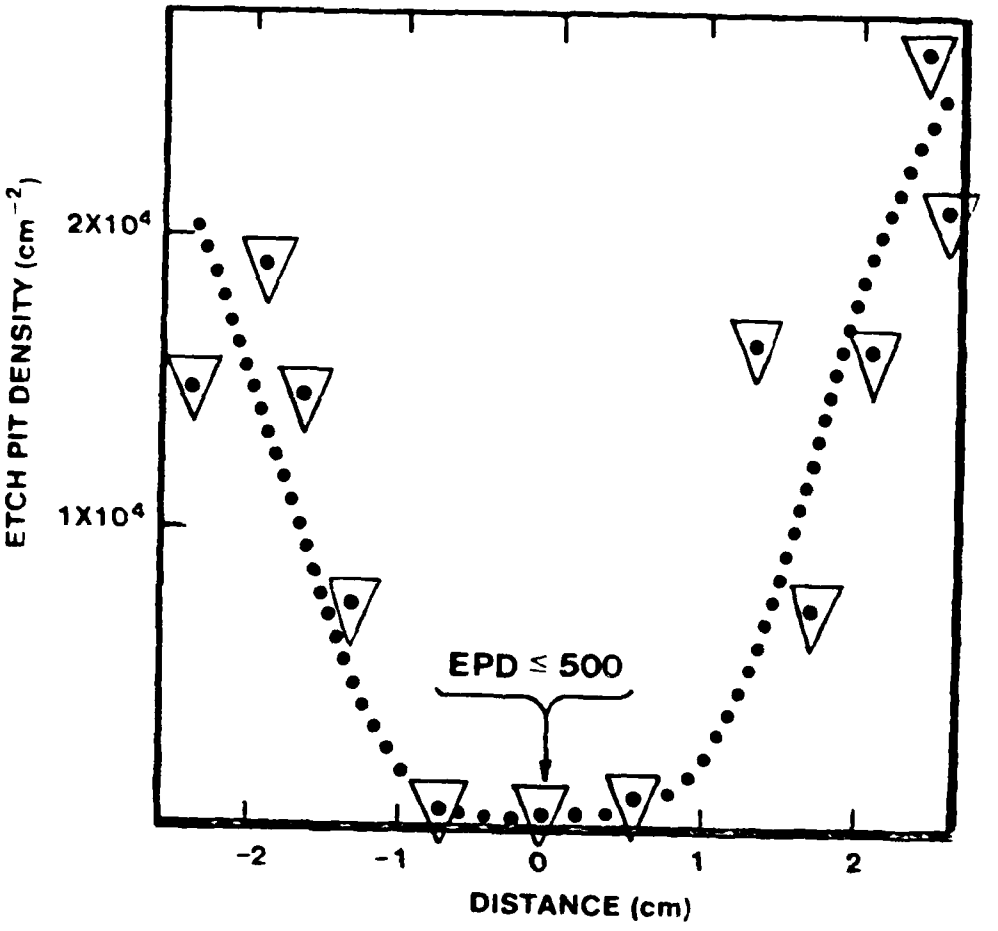


Figure 2. Distribution of EPD in a 5-cm wafer for an unseeded, single-crystal GaAs showing:

- potential of dislocation free, undoped GaAs.
- U-shaped distribution of EPD.

than 500/cm^2 for the central 2.5-cm column; even near the edges of the wafer the EPD is lower than the values observed for commercially available LEC GaAs. In this crystal, microscopic growth striations were not detectable.

The HEM GaAs growth has been extended from 2-inch to 3-inch-diameter crystals. Similar uniformity has also been observed in these crystals[11]. Figure 3 shows the variation of EL2 concentration both in the radial and axial direction of a 3-inch-diameter HEM grown GaAs crystal. Comparable uniformity has not been observed for commercially available GaAs crystals. This uniformity of properties in HEM GaAs is attributed in part to the *in situ* whole ingot annealing which is part of the processing cycle for HEM growth. In addition to uniformity of properties, it has been shown that semi-insulating GaAs can be grown by HEM without doping[10]. This has been achieved even though silica crucibles have been used for HEM growth.

In the recent growths of 3-inch-diameter HEM GaAs crystals, twinning was observed in the structure. This twinning is associated with non-optimized seeding conditions near the outer edge of the seed. While this twinning is observed in 3-inch-diameter crystals, there is no theoretical reason for this condition to exist.

It has been demonstrated that low temperature gradients and prolonged post-solidification annealing are easily accomplished by the HEM process. When applied to GaAs crystal growth, this can lead to low dislocation density and uniform properties without doping. The resulting crystals have shown no observable

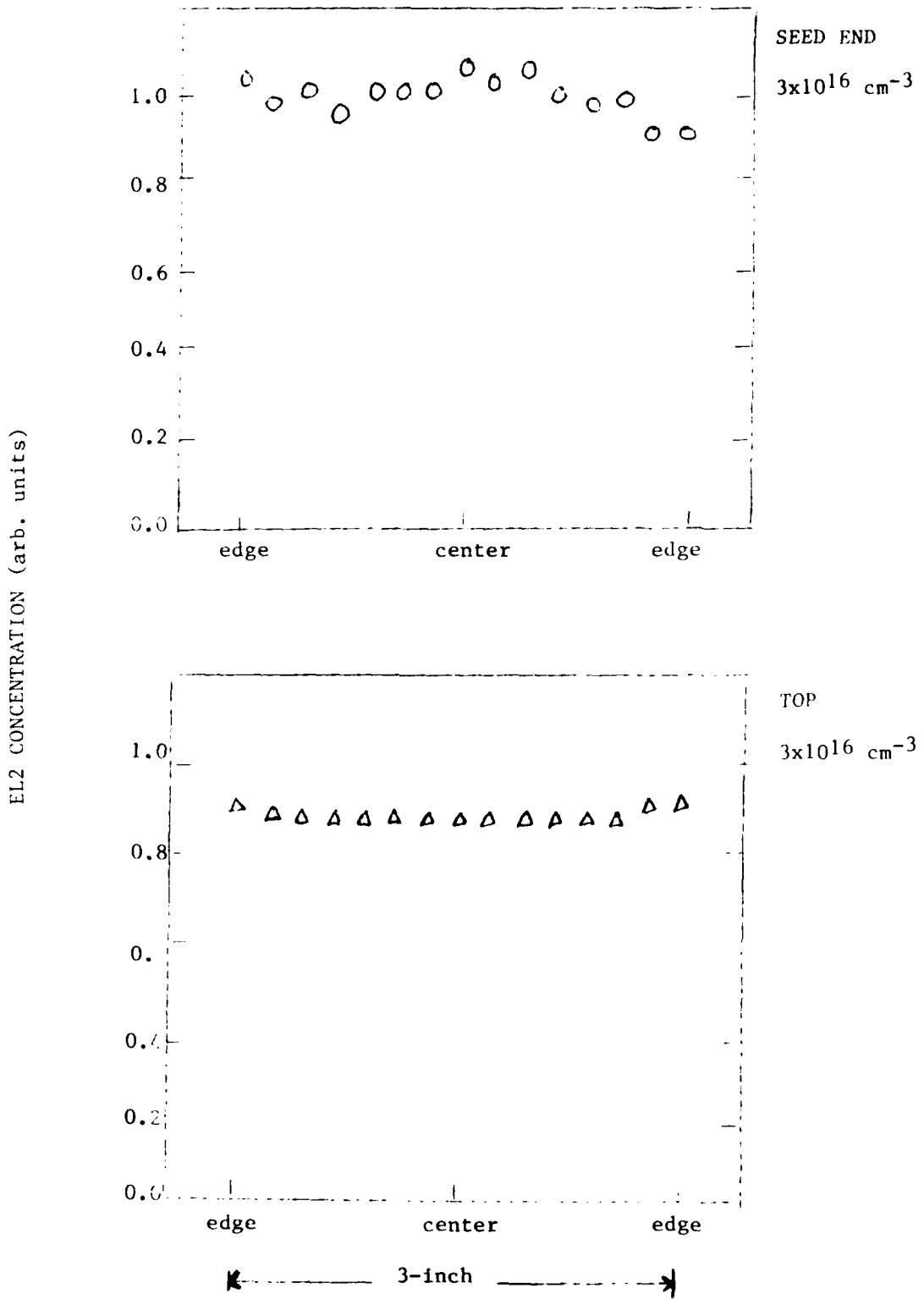


Figure 3. Uniformity of EL2 concentration across a wafer as well as within a 7.5-cm-diameter GaAs boule.

growth striations. These features make HEM a promising method for growth of large diameter GaAs crystals for microwave device applications.

During the initial stages of 3-inch-diameter HEM crystal growth, the uniformity of properties has been demonstrated; however, twinning has been observed in the structure of (100) GaAs crystals associated with non-optimized seeding conditions. This program is to investigate twinning and lineage behavior and develop seeding conditions to eliminate it and allow growth of 3-inch-diameter GaAs crystals with uniform properties. HEM crystals have the potential to have very low dislocation density without the use of dopants.

2.2 The Heat Exchanger Method (HEM™)

The Heat Exchanger Method (HEM™) is being used for the commercial production of 10-inch-diameter sapphire crystals. These crystals are of very high quality and it is possible to grow sapphire by HEM free of scattering centers for stringent optical applications. HEM is also in commercial production for multi-crystalline silicon ingots for photovoltaic and optical applications. A number of mixed oxides, fluorides and compound semiconductors have also been grown by HEM.

The salient features of the process are shown in Figure 4. The crucible with the seed positioned at the bottom is loaded with charge and placed on top of the heat exchanger. After evacuation, heat is supplied by the graphite heater and the charge is melted. The seed is prevented from melting by forcing gaseous helium through the heat exchanger.

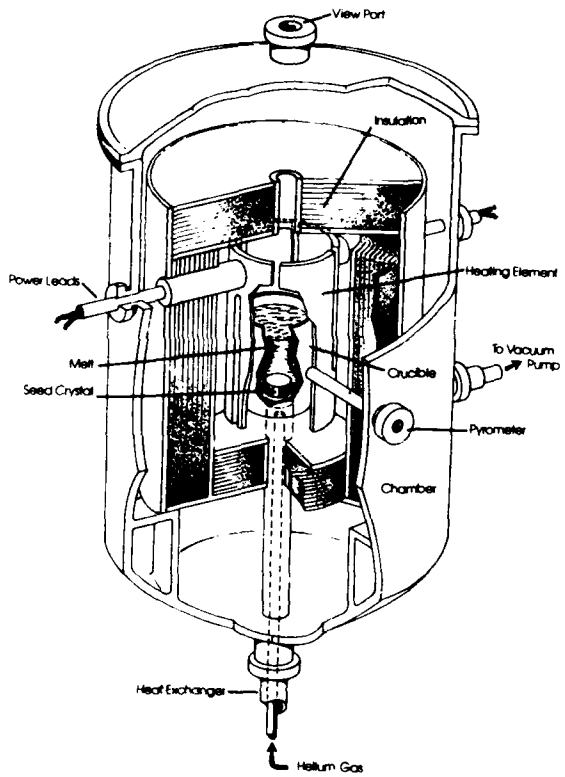


Figure 4. Schematic of an HEM furnace.

Growth is started after sufficient meltback of the seed is achieved by increasing the flow of helium and thereby decreasing the heat exchanger temperature. The liquid temperature gradients are controlled by the furnace temperature, while the temperature gradient in the solid is controlled by the heat exchanger temperature. Crystal growth is achieved by controlling the heat input as well as the heat extraction. After solidification is complete, the gas flow through the heat exchanger is decreased to equilibrate the temperature throughout the crystal during the annealing and cooldown stage.

The HEM is the only crystal growth process in which both the heat input and heat extraction are controlled. The independent liquid and solid temperature gradients are achieved without movement of the crucible, heat zone or crystal. After the crystal is grown, it is still in the heat zone and can be cooled at a controlled rate to relieve solidification stresses. This unique capability allows the growth of sapphire up to 32-cm diameter and weighing about 50 kg without cracking due to thermal stresses associated with such large sizes.

A distinguishing feature of the HEM, as compared with Czochralski (Cz) or top-seeded processes, is that the solid-liquid interface is submerged beneath the surface and is surrounded by the melt. Under these conditions the thermal and mechanical perturbations are damped out by the surrounding molten mass before they reach the interface. This results in uniform temperature gradients at the interface. In the Cz process and top-seeded techniques, growth occurs at the melt surface where

the local gradients vary sufficiently to cause solidification and remelting of the crystal. Precise control of the furnace and heat exchanger temperatures, combined with minimized thermal perturbations resulting from the submerged interface, gives HEM a big advantage over the other growth techniques.

In the HEM growth, after the crystal is grown, the temperature of the furnace is reduced to just below the solidification temperature and the helium flow is reduced at a desired rate. The whole crystal can therefore be brought to high temperatures to anneal the solidification stresses, followed by uniform cooling at a controlled rate to room temperature. Because *in situ* annealing is part of the solidification cycle, HEM can reduce the defect density. Further, the last and most impure material to solidify is along the crucible walls, where it can be removed. These features of HEM produce uniform growth and the only sapphire free of light scatter.

In the case of sapphire and silicon, we have demonstrated that once crystal growth parameters are established, large crystals can be grown.

The HEM is currently being adapted for the growth of $Ti:Al_2O_3$, $Cr,Nd:Gd_3Sc_2Al_3O_{12}$ (Cr,Nd:GSAG), GaAs, CdTe, $Co:MgF_2$, aluminum oxynitride (ALON) and BaF_2 crystals.

From an economic point of view, HEM is cost competitive. The furnace is uncomplicated, automated, and well insulated, which results in low equipment, labor and energy costs.

3.0 Experimental Results

GaAs crystal growth in HEM was carried out in sealed silica crucibles using a single crystal seed and presynthesized GaAs meltstock, without the use of any encapsulant. Crystals up to 3-inch diameter were grown. However, spurious nucleation and twins were observed in the structure as a result of non-optimized seeding conditions. The "seeding" in HEM cannot be observed because the solid-liquid interface is submerged and optimization must be achieved with successive growth experiments. In the HEM parameters are programmed in a microprocessor and can be reproduced.

Prior to growing crystals for the program, an experimental HEM furnace was set up to permit crystal growth under higher temperature gradients. Silica crucibles and appropriate graphite retainers were designed and fabricated to carry out efficient directional solidification.

During crystal growth it is necessary to balance the vapor pressure of arsenic inside the sealed crucible with the pressure in the heat zone to maintain the integrity of the crucible. This balance of pressure is dependent on the furnace temperature.

Crystal growth parameters were developed to achieve sufficient meltback of the seed and uniform growth. After solidification was completed annealing and cooldown parameters were developed. The crystals grown were characterized for structure, resistivity, carrier concentration, mobility and EL2 concentration. The details of the experimental effort are given in the following sections.

3.1 HEM Furnace Preparation

An experimental HEM furnace with a graphite heat zone and graphite felt insulation was used for the experimental program. This furnace is capable of operating under pressure up to 60 atm or under vacuum. A molybdenum heat exchanger was inserted from the bottom of the furnace and a helium gas flow control system was used to control the heat exchanger temperature. This furnace was used prior to this program for the growth of 3-inch-diameter GaAs crystals. Appropriate changes were made to the heat exchanger system to increase the range of temperature gradients available for crystal growth. The graphite element was heated resistively using a three-phase ac power supply. Appropriate instrumentation exists on the furnace so that the crystal growth parameters can be controlled, monitored and regulated during the experiments. Prior to crystal growth the experimental furnace was baked out to approximately 1350°C under vacuum to purify heat zone.

3.2 Silica Crucibles and Graphite Retainers

Silica crucibles for 3-inch-diameter GaAs crystal growth were redesigned so that efficient crystal growth could be carried out under higher temperature gradients in the solid. The crucibles were received in two parts. The parts were etched in 10 percent HF solution and rinsed with DI water, followed by rinsing with methanol. After drying the crucible, a single crystal GaAs seed was placed at the bottom of the crucible and the crucible was loaded with approximately 1.2 kg of

presynthesized GaAs meltstock. The top portion of the crucible was sealed to the bottom portion with a flame and the crucible was evacuated with a vacuum pump. The crucibles were evacuated and backfilled several times before sealing.

At the melting point of GaAs, silica is soft, and it is necessary to support the crucible with graphite retainers that were specially designed and fabricated for the 3-inch-diameter crucibles. These graphite parts were fabricated from purified graphite and baked out under vacuum in the HEM furnace at high temperatures prior to use.

3.3 Heat Flow

The HEM furnace is very well insulated so that the heat input is from the heating element and the heat extraction is primarily through the heat exchanger. A schematic of the heat flow is shown in Figure 5. For the charge the primary heat input is through the walls of the crucible and the heat extraction is through the center portion of the bottom. Under these conditions the temperature gradients in the liquid are controlled by the furnace temperature and the temperature gradients in the solid are controlled by the heat exchanger temperature. During the growth cycle these temperatures can be controlled independently so that the temperature gradients in the liquid and solid can be varied. This control of temperature gradients is unique to the HEM and is achieved without movement of the crucible, heat zone or heat exchanger. By changing the temperature gradients during the growth stage, the shape of the solid-liquid interface can be varied.

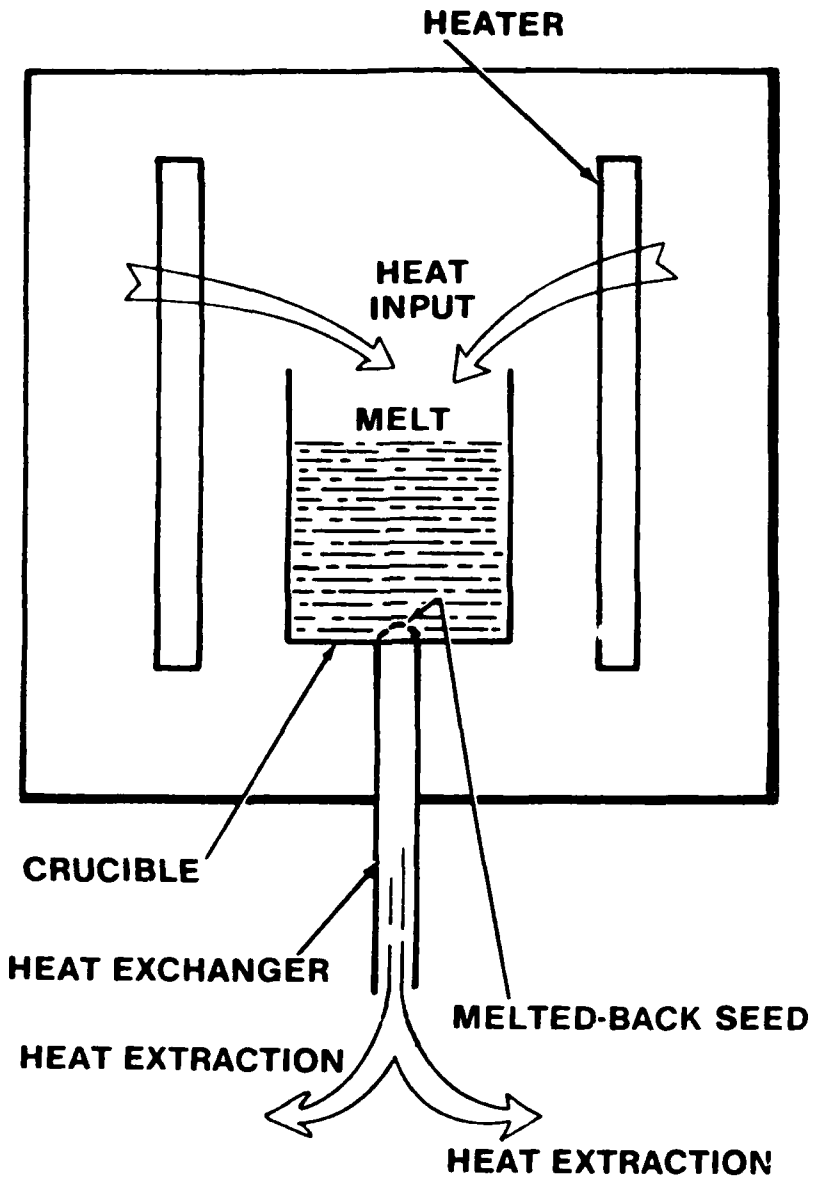


Figure 5. Heat flow diagram in HEM.

A heat flow analysis was carried out on an IBM PC XT using LOTUS 1-2-3 software. The technique used was to apply spreadsheet programs to finite element analysis as described by Dobson and Wolff[18]. To perform the analysis, the derivatives of the function are expressed as difference equations of the function at finite intervals. For each point on the interval, or node, a finite difference equation is written. Boundary conditions are included and together these result in a set of simultaneous equations which can be solved numerically at each node. Several iterations of the program are then required to solve all the equations.

The analysis used is based solely on steady-state conduction. This assumption is valid because at the growth temperatures of GaAs, conduction is expected to be the primary heat transfer mechanism. Convection is not considered in the model of heat flow analysis; convection is minimized in HEM growth because of stabilizing temperature gradients. The model did not incorporate data on thermal conductivity as a function of temperature; in the range of growth temperatures of GaAs this change is small. The model does not allow changes in phase; only one phase is assumed. This assumption is not valid because during growth the liquid and solid phases coexist and the conductives are much different. To simplify the analysis, all nodes were assumed to be of the same thickness. This simple model is not expected to yield precise data; however, it is useful in evaluating trends.

Figure 6 shows three cases of changes in interface shape expected in the HEM when GaAs growth is carried out under high, medium and low temperature gradients in the liquid. The growth and curvature of the solid-liquid interface can be altered by changes in the temperature gradients. These data have been used to make appropriate changes in crystal growth parameters so that single crystal growth can be achieved and spurious nucleation minimized.

To obtain more precise data, it is necessary to modify the simple heat flow analysis. This is not within the scope of the present program.

3.4 Crystal Growth

During the program 10 crystal growth experiments were carried out and the details of these experiments are given in Table 1. For all experiments silica crucibles were prepared and loaded with a single crystal GaAs seed placed at the bottom and covered with presynthesized GaAs meltstock. The crucible was evacuated and backfilled with argon several times prior to sealing. This crucible was supported by a retainer in the HEM furnace. Heat was applied by the graphite resistance heater and the charge was melted. Prior to melting, helium was circulated through the heat exchanger to prevent melting of the seed. The charge was superheated above the meltpoint to the desired level.

During the entire heat up the furnace pressure was monitored so that the pressure inside the crucible and the heat zone was balanced to prevent crucible distortion. After stabilization of the melt, temperature gradients in the solid and liquid were

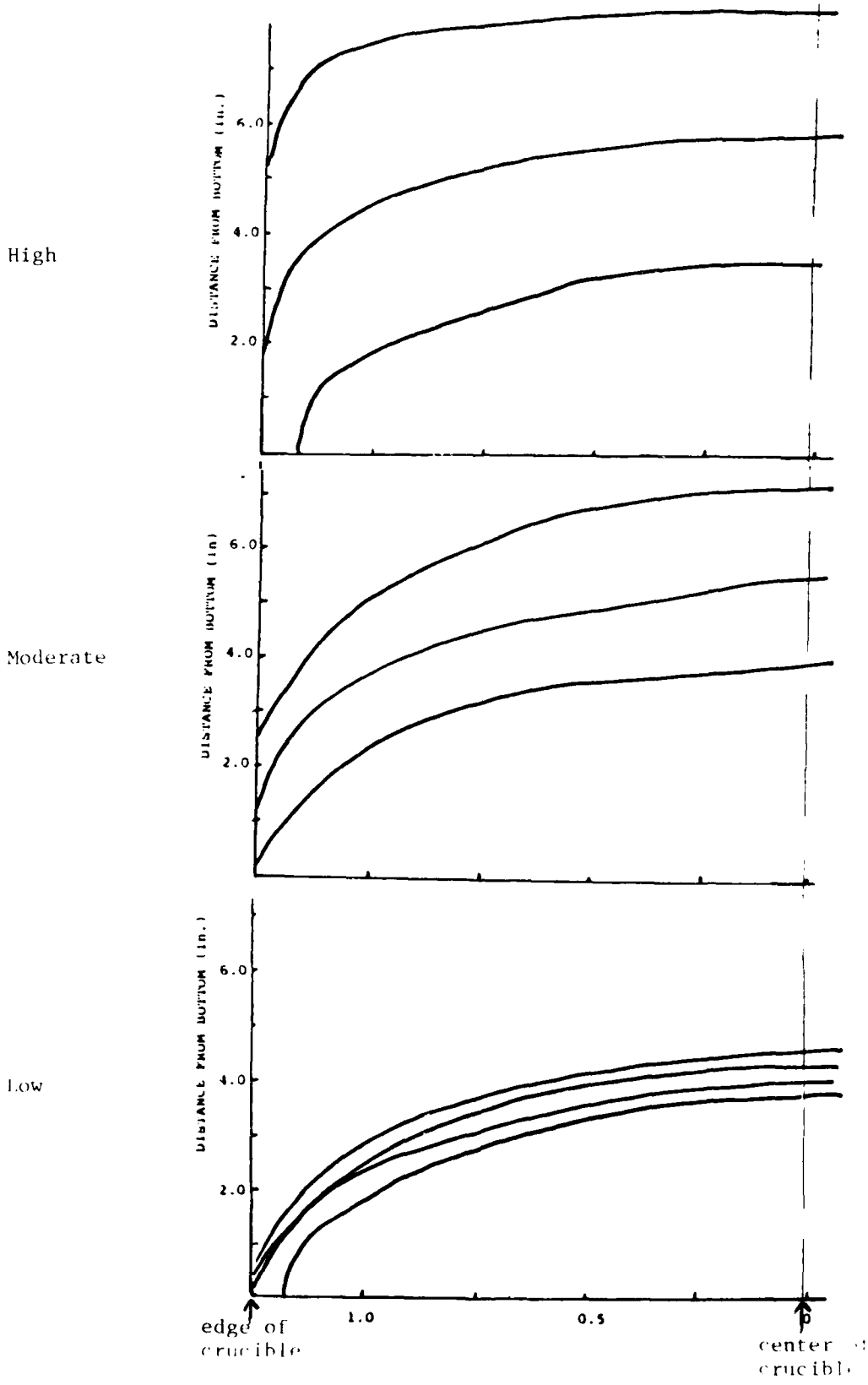


Figure 6. Temperature gradients in the liquid.

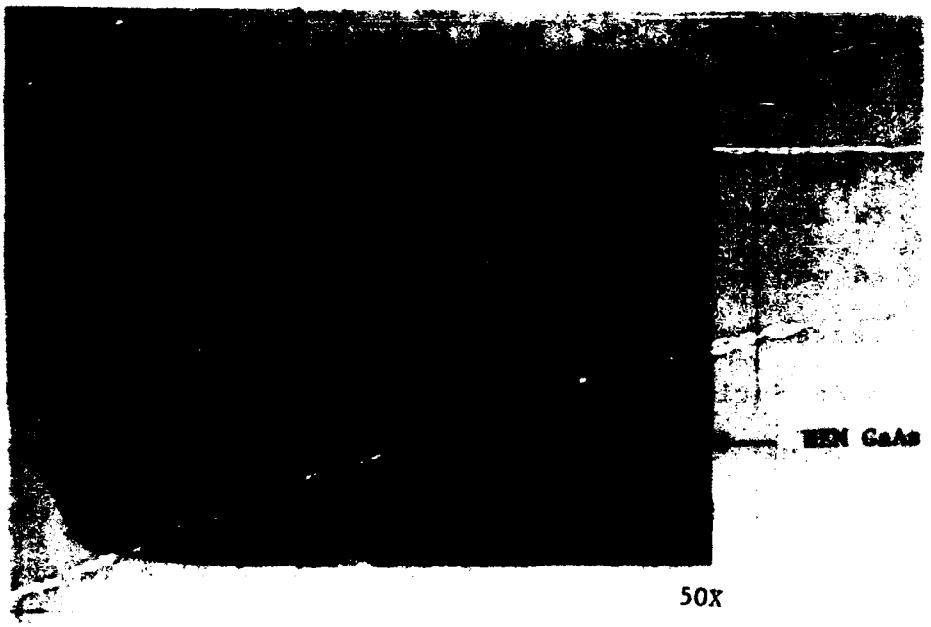
Table 1. Details of experiments for 3-inch-diameter GaAs crystal growth by HEM.

Exp. No.	CSI No.	Charge Wt. (gms)	Superheat °C	Stabilization Time (hrs.)	Growth Time (hrs.)	Cooldown Time (hrs.)	Remarks
1	101	1312	-	-	-	-	Evaluate crucible distortion.
2	102	1225	24	3.0	18	16	No seed meltback. multicrystalline growth.
3	103	1118	35	3.5	18	8	Meltback of seed on top surface only.
4	104	1346	35	3.5	18	16	Twins restricted to the edge of the ingot.
5	107	1200	35	4.5	18	12	Lower temperature annealing.
6	108	1275	40	4.0	18	6	No twins at bottom. Nucleation of a spurious grain.
7	110	1315	40	4.0	20	24	Minimized spurious nucleation at bottom.
8	112	1357	40	4.0	20	10	Initial growth under high liquid temperature gradients.
9	113	1314	40	3.0	23	44	More prolonged growth under high temperature gradients. Improved structure.
10	114	1332	40	3.0	28	44	Lower temperature annealing and slow cooldown; very shiny top surface.

varied so that solidification was achieved. After complete solidification the furnace temperature was reduced and the temperature gradient in the solid was reduced in order to accomplish *in situ* whole-ingot annealing. Thereafter the crystal was cooled at a controlled rate.

Experiment 1 was carried out to evaluate crucible distortion. Data were obtained on pressure inside the crucible and in the heat zone to retain the integrity of the crucible. For this experiment the charge was heated above the melt point and thereafter cooled rapidly.

Experiment 2 was carried out using the data gained from the first run. In this experiment the melt was superheated to approximately 24 degrees above the melting point of GaAs. After stabilization of the melt for 3 hours, temperature gradients in the solid and liquid were varied so that complete solidification was achieved in approximately 18 hours. When solidification was complete, the furnace temperature was reduced and the temperature gradient of the solid was reduced to achieve *in situ* whole-ingot annealing. The ingot was cooled in approximately 16 hours after annealing. The ingot was sectioned, lapped and etched to reveal the structure. Very large multicrystalline GaAs was produced. Examination of the seed section showed that no melt back of the seed had been achieved so that unseeded growth had been initiated. Detailed microscopic characterization of the seed surface showed that during melting the liquid seeped under the seed and lifted it on one side and froze. One of the micrographs showing the seed/melt interface is shown in Figure 7. While the



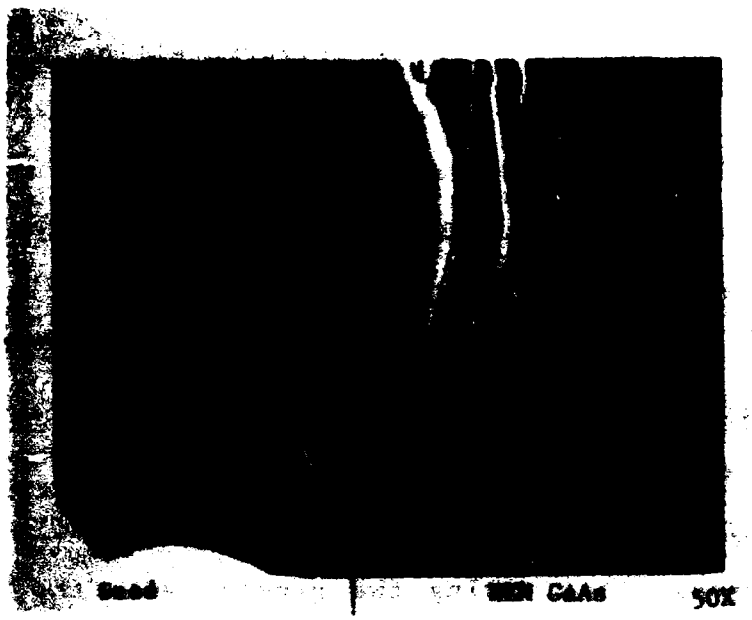


Figure 7. Microscopic examination of two areas of seed-HEM grown GaAs showing no meltback of seed.

crystal growth parameters utilized for Experiment 2 were appropriate when the HEM furnace was configured for lower temperature gradients in the solid, the bottom of the crucible was too cold in the new configuration.

In Experiment 3 procedures similar to Experiment 2 were carried out except that the melt was stabilized at approximately 35°C above the melting point. Changes in temperature gradients were made during the growth cycle, and the ingot was solidified in approximately 18 hours. After annealing, the ingot was cooled down in approximately 8 hours. Figure 8 shows the shiny top surface of the ingot. Twins can also be seen in the structure. Characterization of the ingot showed that the central portion was single crystal with some twins; spurious nucleation had caused the periphery of the ingot to be polycrystalline. Microscopic examination of the seed-growth interface showed that some meltback of the seed had been achieved on the top surface. However, near the edges no meltback was evident. Figure 9 shows these interfaces. In areas where meltback was achieved, a cellular structure corresponding to the seed was reproduced in the grown material. Near the edges of the seed where no meltback was achieved, considerable twinning was observed.

In Experiment 4 procedures similar to Experiment 3 were carried out except that during the growth cycle the temperature gradients were varied to carry out initial growth under higher temperature gradients in the liquid. The top surface of the ingot produced in this experiment is shown in Figure 10. The top portion of the ingot was sectioned, lapped and etched, and the

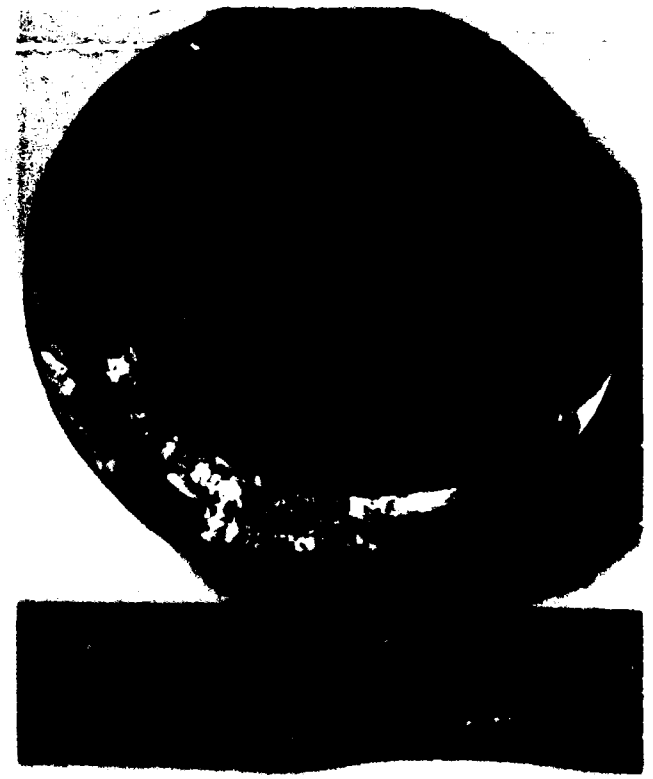
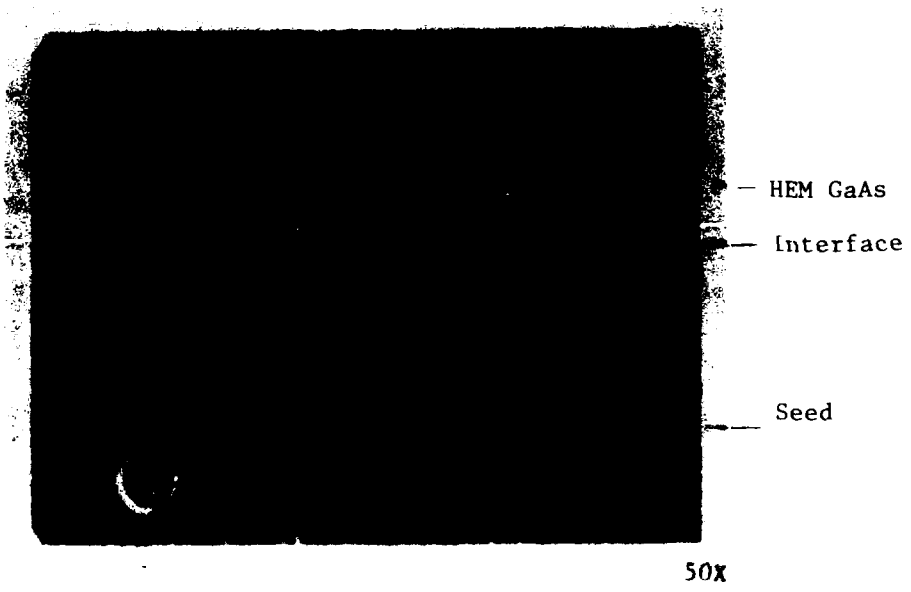
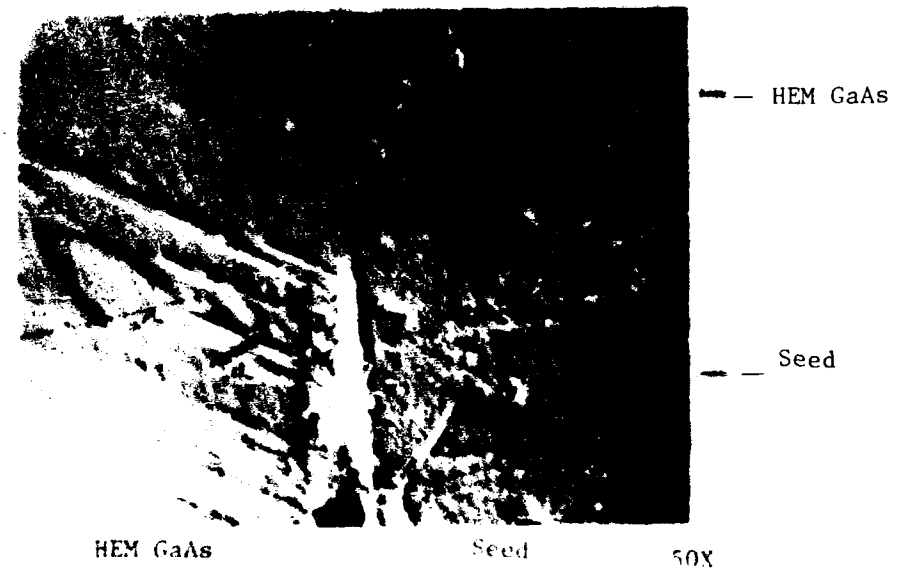


Figure 8. Top surface of HEM GaAs grown in Experiment 3.



(a)



(b)

Figure 9. (a) Melted back seed interface at the top surface of seed.
(b) Twins nucleating from unmelted edge of seed.

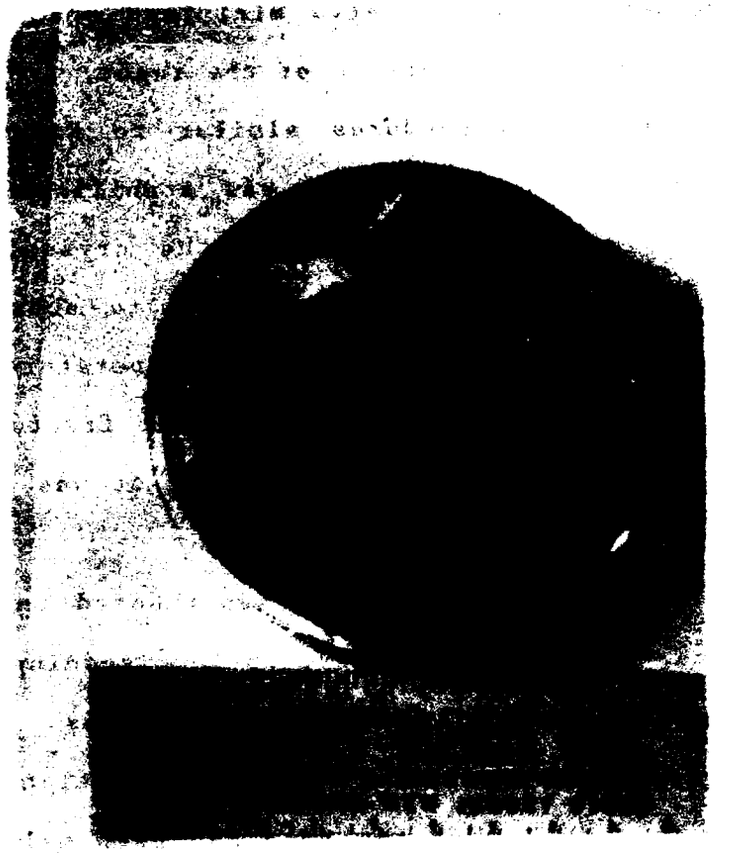


Figure 10. Top surface of ingot produced in Experiment 4.

central area of the ingot was single crystal and twins were visible near the periphery (Figure 11). Detailed examination of the seed-grown interface showed that improved seeding had been achieved. However, some twins had also nucleated. With growth carried out under high liquid gradients, spurious nucleation during the growth stage was also minimized and the twins were pushed toward the outside surface of the ingot.

In Experiment 5 procedures similar to Experiment 4 were carried out except that the melt was stabilized for a longer period. After growth was completed the crystal was *in situ* annealed at approximately 900°C compared to above 1,000°C for earlier experiments. The annealing temperature was changed because we observed that the silica crucible fractures during the cooldown cycle. The structure of this ingot was similar to the earlier experiment.

In Experiment 6 the melt was superheated to approximately 40°C above the meltpoint to achieve optimum seeding and minimized spurious nucleation. Solidification was completed in approximately 18 hours. Microscopic examination of the seed-grown interface showed that the seed had been melted on the top as well as on the sides. The structure of the bottom section of the ingot just above the seed is shown in Figure 12. There is only one small spurious grain nucleated near the edge. The twinning in this section was also minimized. This grain is probably nucleated from the crucible wall and may be caused by a cold spot in the heat zone. The top surface of the ingot is shown in Figure 13. The spurious grain is enlarged in size

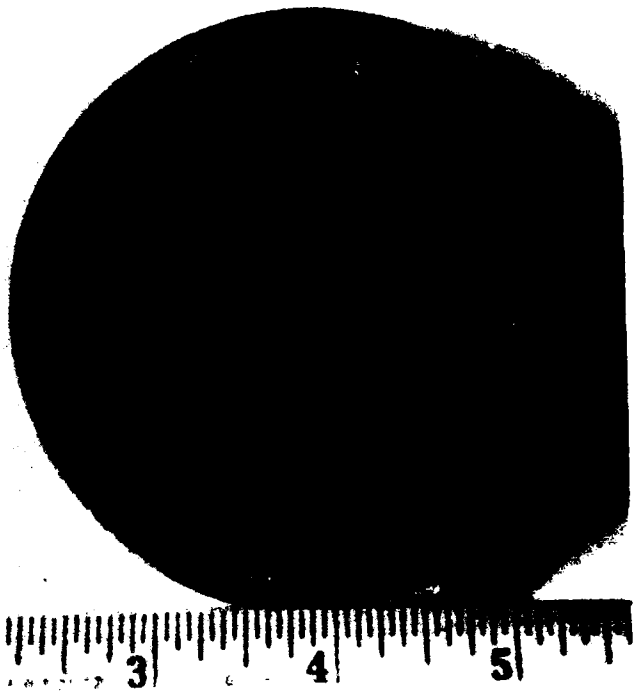


Figure 11. HEM GaAs ingot showing twins restricted to two areas near the edge.

Figure 12. Structure near the bottom of ingot grown in Experiment 6 showing no twins and nucleation of one spurious grain.

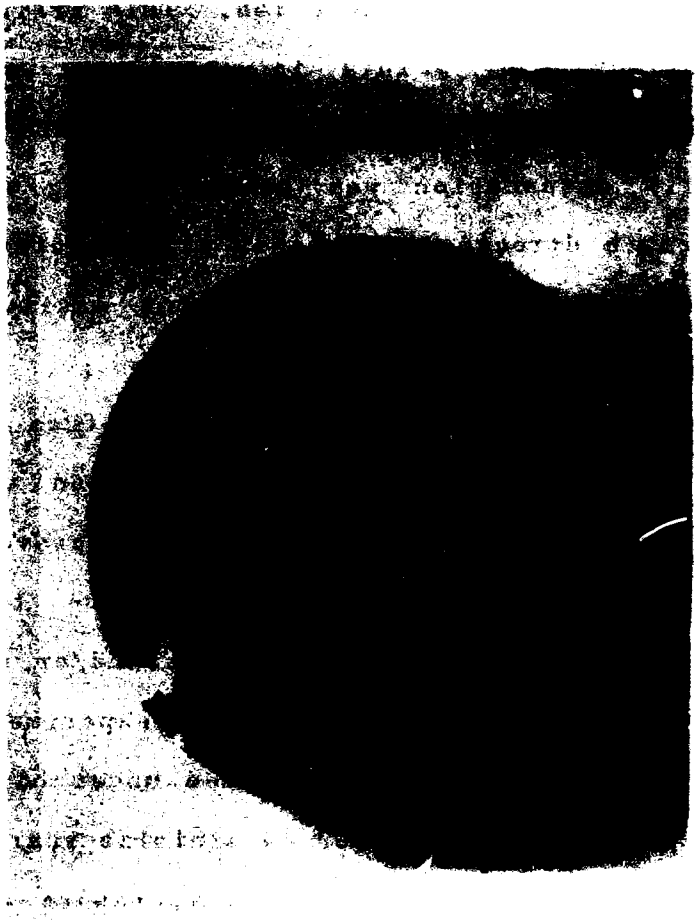
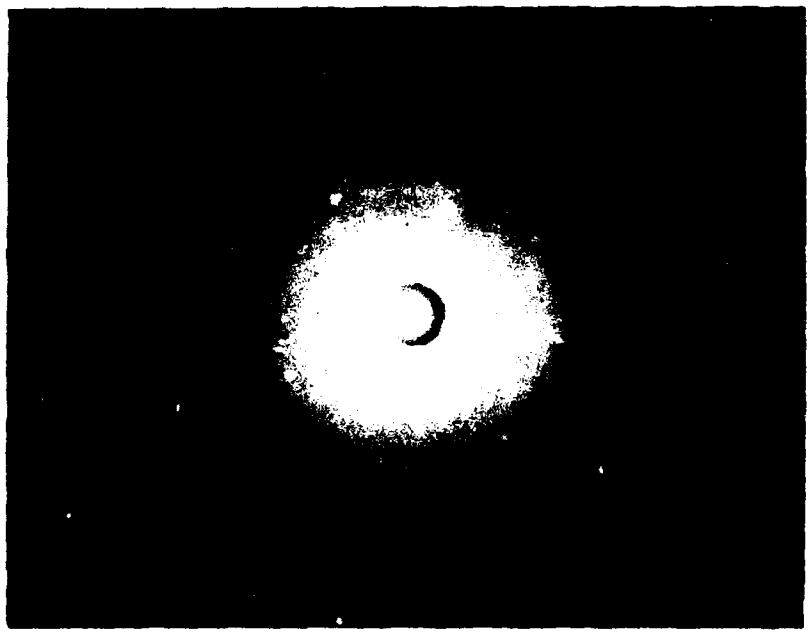


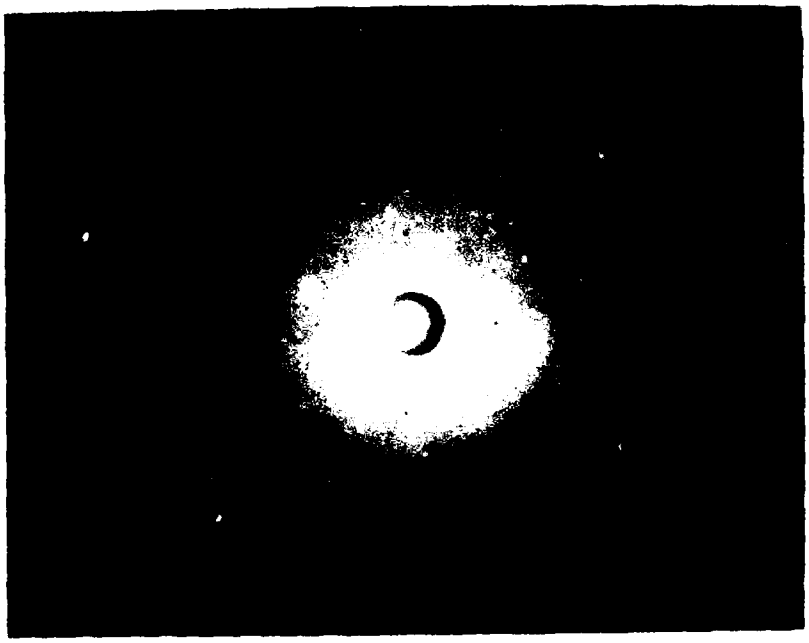
Figure 13. Structure near top of ingot showing that the spurious grain had enlarged with growth.

because of preferential growth compared to (100) orientation and now covers nearly half the surface. A back reflection Laue photograph (Figure 14a) of the main grain from the bottom of ingot 6 showed that it was (100) orientation. The spurious grain was not (100) as shown in Figure 14b. This grain was identified as (221) orientation. This is consistent with the result obtained with unseeded growth of GaAs by HEM[10] where single crystal (221) orientation was grown showing that it is the preferred growth direction. This is also consistent with data[19] on LEC growth whereby (100) orientation easily twins to grow (221) orientation.

The spurious nucleation is originating from the walls of the crucible. This is expected to happen when the solid-liquid interface shape is very flat. In order to prevent the spurious nucleation, it may be necessary to have the solid-liquid interface convex near the crucible wall and/or treat the inside surface of the silica crucible. Further experiments were carried out where initial growth was performed under higher temperature gradients in the liquid in order to minimize spurious nucleation. In these experiments the annealing temperature and the cooldown cycle were varied in order to evaluate their effect on the properties of GaAs. Detailed characterization of the structure of the ingots showed that spurious nucleation was pushed up toward later stages of the growth cycle with progres ive changes in crystal growth parameters. However, the spurious nucleation was not eliminated. Figure 15 still shows the spurious nucleation in the bottom section of ingot 10. However, it is at a later stage of the growth cycle.



(a)



(b)

Figure 14. (a) Main grain at bottom of ingot 6 showing (100) orientation.
(b) Spurious grain in ingot 6 which was identified as (221) orientation.

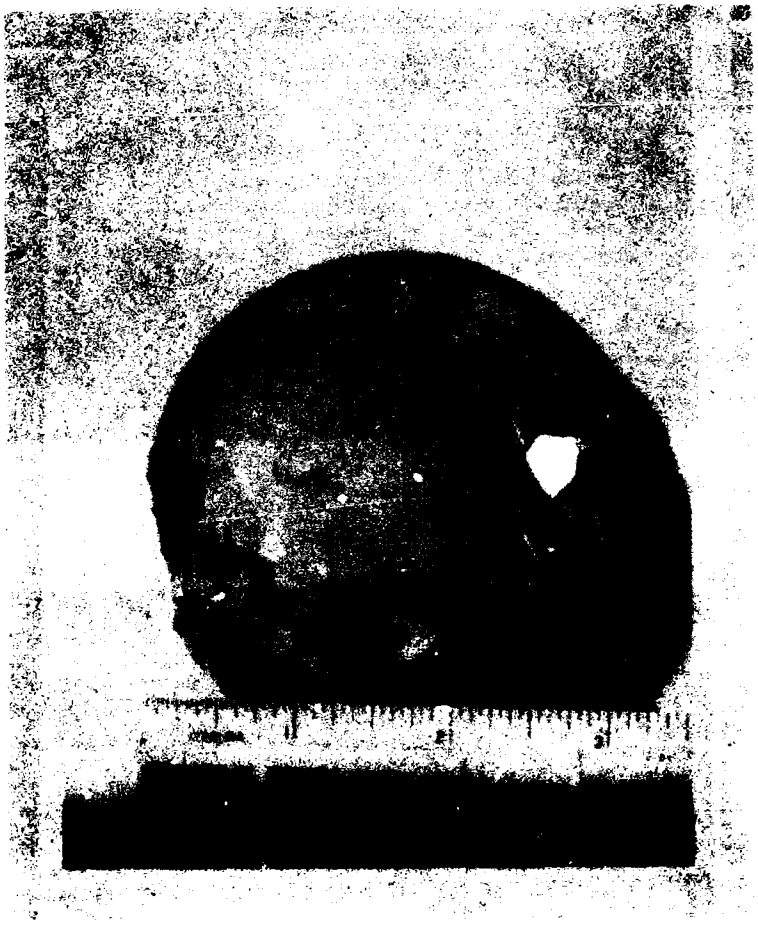


Figure 15. Structure away from the seed end of ingot 10.

3.5 Characterization

It has already been established that HEM is a promising method for producing GaAs for integrated circuits applications. One of the key advantages of the process is to produce very uniform quality material. While uniformity of properties has been demonstrated, twins and spurious nucleation have been observed in the structure. During the present program it was intended to minimize the lineage in the structure and to evaluate the uniformity of properties in the material. The crystals grown during the program were characterized for electronic properties at Spectrum Technology, Inc. using their production processing lines. Samples from HEM-grown GaAs crystals were characterized for carbon concentration, resistivity, mobility and EL2 concentrations and the details are given below.

3.5.1 Carbon Concentration

A sample from an HEM-grown 3-inch-diameter GaAs crystal was characterized for carbon concentration by measuring the Localized Vibrational Mode (LVM) absorption of carbon using Fournier Transform Infrared (FTIR) spectroscopy. A 3-mm-thick sample was cut and polished and prepared for evaluation. Data were obtained for absorbance as a function of wavelength and is shown in Figure 16. These data showed that the carbon concentration in the sample was below the detectability limit as evidenced by the absence of a peak at approximately 580 cm^{-1}. The detection limit of room temperature measurement is about 3×10^{14} atoms/cm^3.

(related resolution for improved S/N)

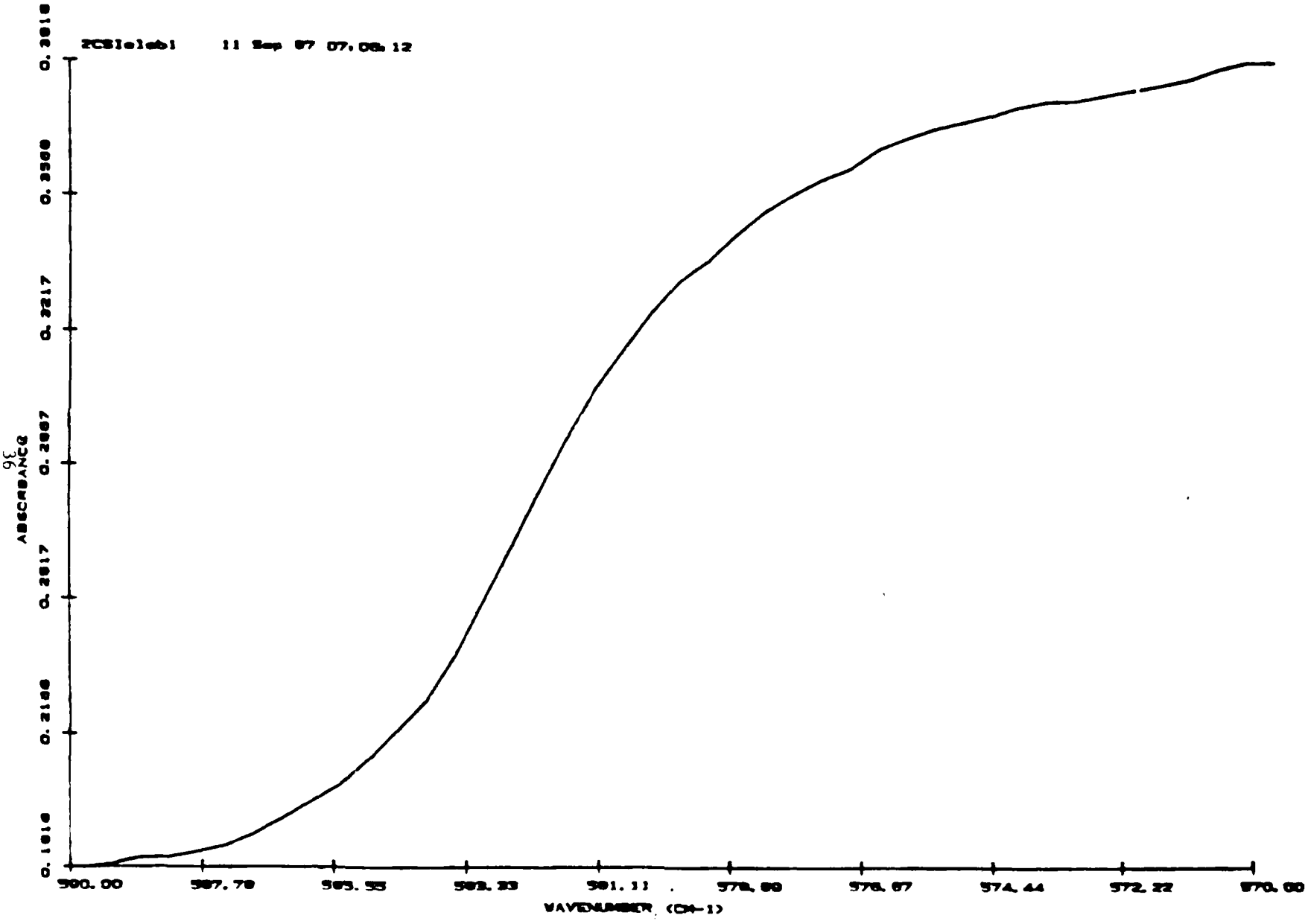


Figure 16. FTIR spectrum of HEM GaAs showing carbon below detectibility limit.

3.5.2 Electronic Properties

A number of samples from HEM-grown GaAs were characterized for resistivity, mobility and carrier concentration. Samples were taken from the seed-end, center; seed-end, periphery; tail-end, center and tail-end, periphery of each ingot in order to evaluate the uniformity of the properties. This sampling approach is consistent with Spectrum Technology's evaluation for their production line GaAs crystals. These characterizations were carried out using the Van der Pauw method (Table 2).

A review of the data in Table 2 shows that within the ingot the properties were uniform. For conducting samples, the mobilities are consistent with the resistivity. The variation of properties within the 3-inch-diameter ingot are similar to smaller 2-inch-diameter HB GaAs. The data for ingot 5 show semi-insulating characteristics. The mobility values of above 7,000 $cm^2/V.sec$ for this material are on the high side of the state-of-the-art LEC samples. These high values for mobility on HEM GaAs are attributed to the very low carbon concentration of the material.

The small variation of properties from ingot-to-ingot is attributed to *in situ* annealing and cooldown parameters. When the ingot was annealed at temperatures above 900°C or cooled rapidly, conducting GaAs was obtained; otherwise, semi-insulating ingots were produced.

Samples from Experiment 3 and Experiment 4 were cut and polished for mapping of EL2 concentration. These samples of approximately 3.8 mm thickness were processed (Figures 17 and 18). The average value for EL2 concentration for the sample

from Experiment 3 was $1.34 \times 10^{16}/cm^3$ with a standard deviation of 8.37 percent. For Sample 4 the mean EL2 value was $1.58 \times 10^{16}/cm^3$ with a standard deviation of only 1.2 percent. These data shows that there is remarkable uniformity of EL2 concentration in HEM GaAs. Another feature observed from Figures 17 and 18 is that there is no preferred EL2 concentration with orientation which is characteristic for LEC material.

3.5.3 Breakdown Voltage

An instrument which measures breakdown voltage which had been previously designed and fabricated by Dr. Jack Lagowski of MIT for Crystal Systems, Inc. This instrument is useful for measuring bulk GaAs samples and estimating the resistivity of the material which is very reliable for evaluation when the sample is semi-insulating. A gold probe is used to measure the breakdown voltage and the instrument is calibrated so that 250 volts corresponds to semi-insulating ($\rho > 10^7$ ohm-cm) behavior. Ingots were characterized for breakdown voltage, and these data were also correlated with the data from the Van der Pauw method. For example, ingot 5 showed semi-insulating characteristics by a breakdown voltage, and this was confirmed with the data in Table 2. Data on ingots from Experiments 9 and 10 also showed semi-insulating characteristics.

Table 2. Characterization of electronic properties of 3-inch-diameter HEM GaAs.

Exp. No.	Sample	Resistivity, ρ (ohm-cm)	Mobility, μ (cm^2/V.sec)	Carrier Concentration, n (cm^{-3})
3	seed-end, center	0.0225	4,890	5.6×10^{16}
	seed-end, ring	0.0219	5,100	5.6×10^{16}
	tail-end, center	0.0135	4,240	11.0×10^{16}
	tail-end, ring	0.0148	4,620	9.3×10^{16}
4	seed-end, center	0.0364	5,050	3.4×10^{16}
	seed-end, ring	0.0350	5,170	3.5×10^{16}
	tail-end, center	0.0180	4,450	7.8×10^{16}
	tail-end, ring	0.0201	4,730	6.6×10^{16}
5	seed-end, center	2.6×10^{7}	6,950	3.5×10^{7}
	seed-end, ring	2.5×10^{7}	7,040	3.5×10^{7}
	tail-end, center	1.3×10^{7}	6,098	8.0×10^{7}
	tail-end, ring	1.0×10^{7}	5,823	1.1×10^{8}
6	seed-end, center	0.0348	4,250	6.3×10^{16}
	seed-end, ring	0.0358	5,220	3.4×10^{16}
	tail-end, center	0.0309	4,701	4.3×10^{16}
	tail-end, ring	0.0326	4,928	3.9×10^{16}
7	seed-end, center	0.349	6,140	2.9×10^{15}
	seed-end, ring	contact problems.		
	tail-end, center	0.144	5,650	7.7×10^{15}
	tail-end, ring	0.140	5,217	9.4×10^{15}

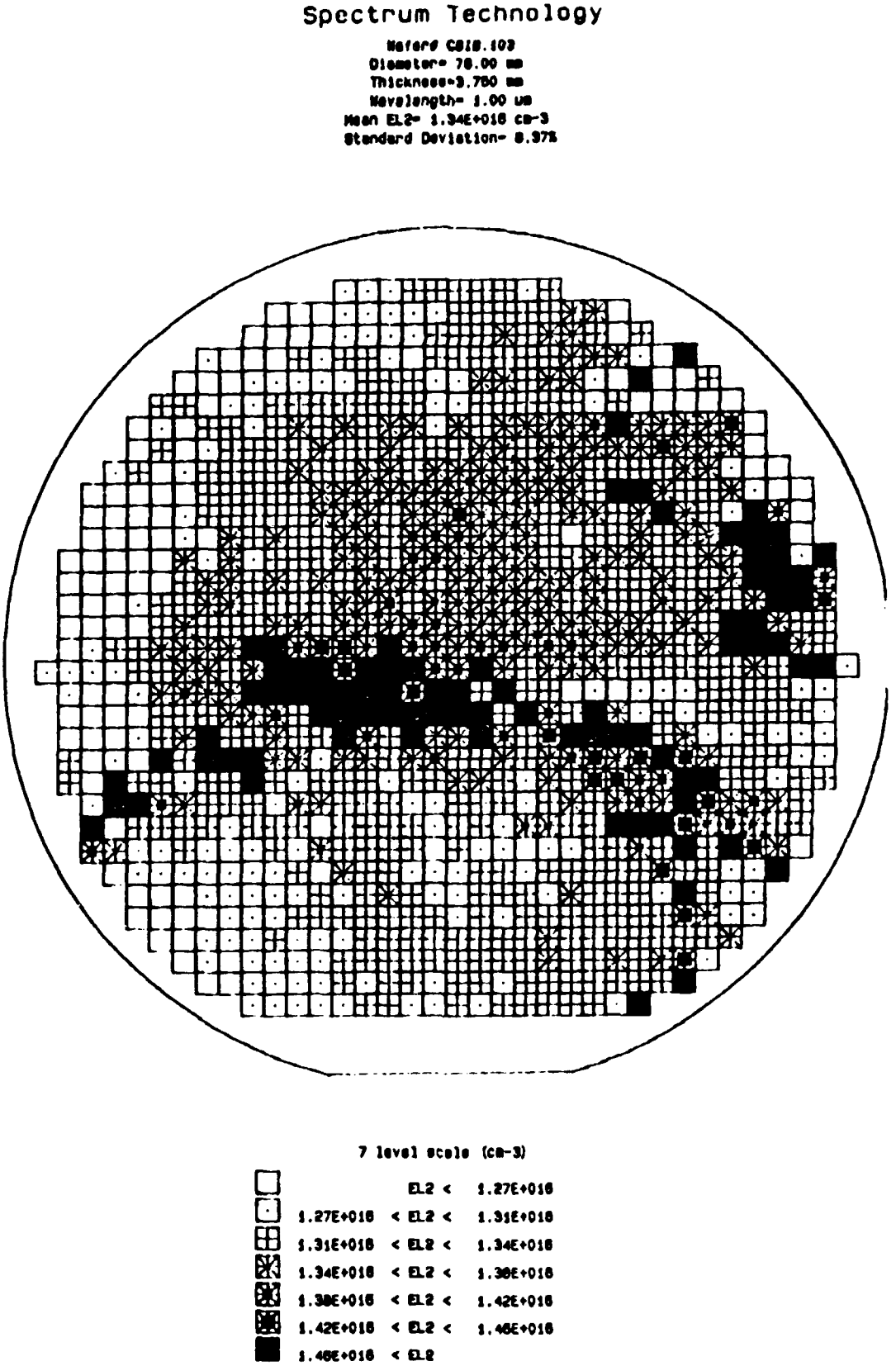
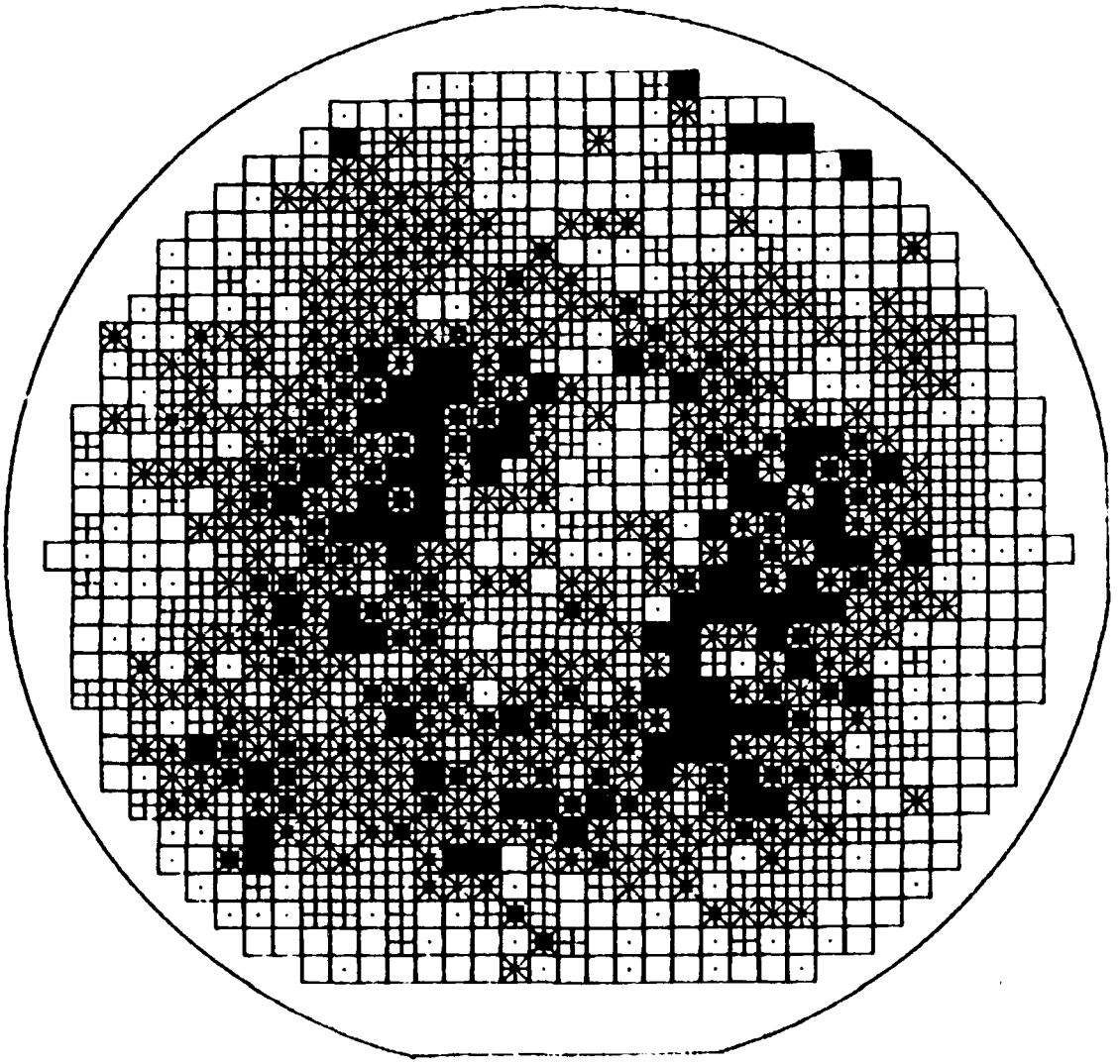


Figure 17. Mapping of EL2 concentration for a 3-inch diameter from Experiment 3.

Spectrum Technology

Wafer# CSIB.104
Diameter= 76.00 mm
Thickness=3.840 mm
Wavelength= 1.00 um
Mean EL2= 1.58E+016 cm-3
Standard Deviation= 1.20%



7 level scale (cm-3)

EL2 <	1.57E+016
1.57E+016 < EL2 <	1.58E+016
1.58E+016 < EL2 <	1.58E+016
1.58E+016 < EL2 <	1.59E+016
1.59E+016 < EL2 <	1.60E+016
1.60E+016 < EL2 <	1.60E+016
1.60E+016 < EL2	

Figure 18. Mapping of EL2 concentration for a sample from Experiment 4.

4.0 Conclusions

Undoped (100) orientation, 3-inch diameter, semi-insulating GaAs ingots have been grown by HEM. These ingots have been grown in sealed silica crucibles using presynthesized GaAs meltstock. Nearly single crystal structure was obtained; however, twins were also observed. The source of these twins has been identified with non-optimized "seeding." In HEM, because of submerged solid-liquid interface, seeding has to be optimized by experimentation. With improved "seeding" conditions, twins originating from the seed were eliminated.

Spurious nucleation from the crucible was also observed. These grains of (221) orientation grew preferentially over (100). When initial crystal growth was carried out under higher temperature gradients in the liquid, the spurious nucleation was pushed toward later stages of the growth.

Samples from HEM GaAs ingots were characterized for electronic properties. Remarkable uniformity of resistivity, mobility and carrier concentration has been observed in the axial as well as radial direction within the ingots. For conducting GaAs, mobilities up to 6,140 $cm^2/V.sec$ have been measured. These values are higher than HB GaAs, and the variation in 3-inch HEM GaAs is similar to smaller 2-inch D-shaped wafers grown in the industry.

Semi-insulating HEM GaAs has shown mobilities higher than 7,000 $cm^2/V.sec$ which is higher than state-of-the-art LEC GaAs crystals. The higher values are attributed to very low carbon concentration ($< 3x10^{14}$ $atoms/cm^3$) in HEM GaAs. Undoped, semi-insulating GaAs has been produced even though the crystals are

grown in silica crucibles. *In situ* annealing in HEM must be carried out at approximately 900°C and the crystal must be cooled at a controlled rate to produce semi-insulating GaAs. EL2 values of $1.58 \times 10^{16}/cm^2$ with a standard deviation of only 1.2 percent have been achieved in 3-inch-diameter HEM GaAs.

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